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SOME PHYSICS OF THE GRUNEISEN PARAMETER
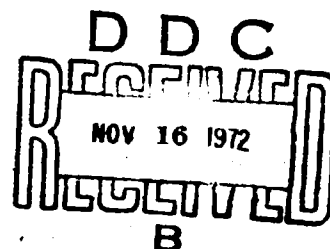
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The separate electron and phonon contributions for metals are considered, and it is shown that except for very high and very low temperatures the phonon contribution dominates. Procedures for evaluating Γ from shock-Hugoniot data for isotropic solids are treated, and the necessity for applying ultrasonic data to anisotropic crystals is considered.

The role of the more exotic thermal excitations of solid state physics in determining Γ is mentioned.

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by

Paul Harris

and

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$\mathcal{I}$

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ABSTRACT

The physics of the Grüneisen parameter for solids is investigated from the view of conceptual and physical contributions. The relatively simple physics of a van der Waal's gas is applied to solid densities yielding a Grüneisen $\Gamma \approx 2$.

The separate electron and phonon contributions for metals are considered, and it is shown that except for very high and very low temperatures the phonon contribution dominates. Procedures for evaluating Γ from shock-Hugoniot data for isotropic solids are treated, and the necessity for applying ultrasonic data to anisotropic crystals is considered.

The role of the more exotic thermal excitations of solid state physics in determining Γ is mentioned.

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I. INTRODUCTION

Consider a system having total internal energy E, pressure P, volume V, and temperature T. The Grüneisen parameter, Γ, for that system is defined by

$$\Gamma \equiv V\left(\frac{\partial P}{\partial E}\right)_V ,\qquad (1)$$

where the derivative is to be evaluated at constant volume. As given by the macroscopic (operational) definition of Eq. (1), Γ is a measure of the change in pressure produced by a change in system total energy under the condition of constant volume.

As evidenced from the above definition Γ is a thermo (energy)-mechanical (pressure) quantity, and as such is expected to be important to thermomechanical problems. A few examples of such problems are: shock wave effects (e.g., explosively driven shock waves in solids), the thermal expansion of solids, and the rapid heating of materials due to their absorbing intense pulses of nuclear radiation. In the last example Γ becomes of extreme importance since, for radiation pulse duration small compared to relevant times for acoustic transport, the induced thermal pressure is directly proportional to Γ.

In this report we shall consider the physics, sometimes on a microscopic scale, responsible for the Grüneisen parameter having its observed values. There is good reason for doing so. Presently, in the United States, technology has outpaced science to the point where design engineers frequently find themselves using materials which have unknown responses to the environments in which they are to be placed. This is especially true in the area of military

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missile technology where very often new exotic materials are required to survive
radiation environments in which their response is unknown. Knowledge of the
Grüneisen constant physics would allow an engineer to make valid estimates for
those materials for which Γ has not yet been measured.

Understanding the physics of Γ is also quite important to the understanding
of related physics problems. One such problem area of interest is that of
electromechanical shock effects in metals. If one analyzes shock propagation
in metals in terms of a two fluid model of electrons and phonons, then the
Grüneisen parameter of each component becomes important. Some of the analysis
presented in this report will be directed towards that problem.

So that the uninitiated reader may be eased gently into the problem we will
begin by treating the relatively simple problem of the Grüneisen parameter of gases.
After that we will consider some generalities of Γ, in particular as they apply
to solids. Finally, calculations will be made of the Grüneisen parameter for some
real systems of interest.

II. GASES

A. **Perfect Gases.**

Consider an ideal monatomic gas with equation of state (EOS) and total energy E given by

$$PV = NkT, \qquad E = \tfrac{3}{2} NkT, \qquad (2)$$

$$\therefore \ PV = \tfrac{2}{3} E . \qquad (3)$$

From Eqs. (1) and (3) we find

$$\Gamma \ (\text{ideal gas}) = \tfrac{2}{3} . \qquad (4)$$

In the above N is the number of molecules (atoms for a monatomic gas), k is the Boltzmann constant (1.38 x 10^{-16} ergs/°Kelvin), and T is the absolute temperature.

Looking now at a gas made up of diatomic molecules with $E = \tfrac{5}{2} Nkt$ we find $\Gamma = \tfrac{2}{5}$. Consequently, a given amount of energy introduced into a diatomic gas produces less of a pressure increase than in the corresponding monatomic gas. This result is easy to understand; for the diatomic case some of the energy goes into the internal energy associated with molecular vibration.

While the above example is somewhat trivial there is information of interest contained in it because the diatomic gas has a hint of solid state behavior in it by virtue of its internal energy. Suppose that we were able to put the energy into the diatomic gas system in a time small compared to that necessary for transitions

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between the translational states of a diatomic molecule. Since $E = \frac{5}{2} NkT$ is composed of $\frac{3}{2} NkT$ kinetic energy associated with translational motion of the center of mass of each molecule, and NkT internal energy associated with vibrational states, the Γ for the system would appear as shown in Fig. 1 below.

Figure 1. Grüneisen parameter as a function of time for beam pulse width time t. The time for translation between vibrational states is t_1 .
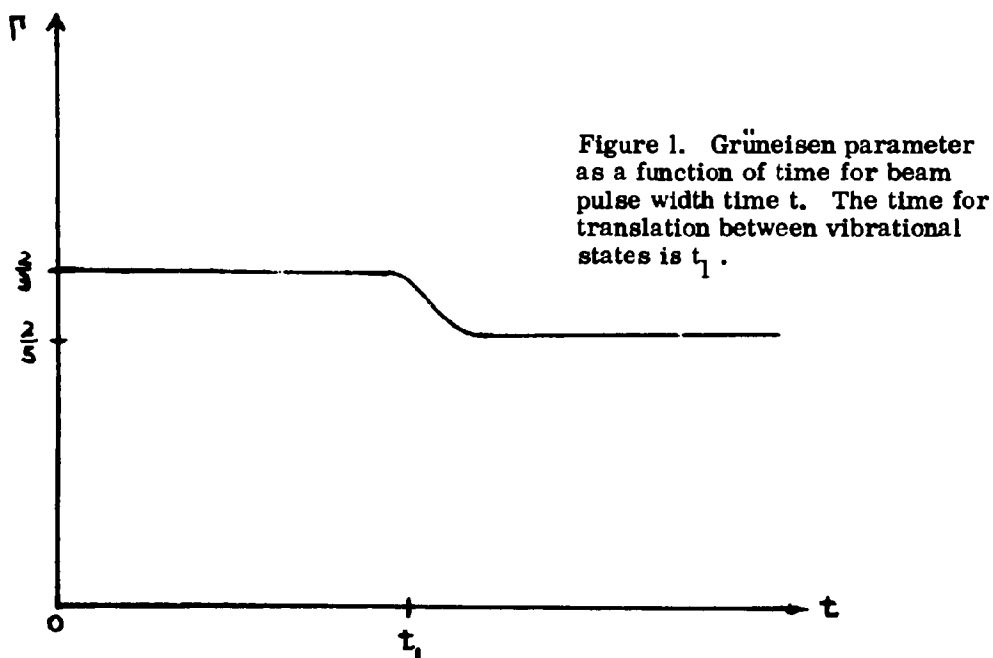
Fig. 1 shows the Γ that would be measured as a function of varying deposition time for the system of diatomic molecules. It is to be understood that we are only talking about a thought experiment here since $t_1 \sim 10^{-14}$ sec. As an alternative to the fast energy pulse the same results (i.e., $\Gamma = \frac{2}{3}$ for a diatomic gas system) can be achieved by imagining an omnipotent hand reaching in and maintaining the pre-radiation separation distance, and thus the pre-radiation state, between the atoms of each molecule.

B. Imperfect Gases.

A gas is considered to be imperfect when interactions between the gas molecules must be considered in order to explain experimental results. One of the simplest models of an imperfect gas is that given by the van der Waals' EOS

$$PV = NkT\left(1 + \frac{Nb}{V} - \frac{Na}{kTV}\right),\qquad(5)$$

$$E = \frac{3}{2}NkT\left(1 - \frac{2Na}{3kTV}\right),\qquad(6)$$

where a and b are constants dependent upon the gas under observation*. The constant b is generally considered as being proportional to the volume occupied by a molecule (and thus unavailable to other molecules), while a is proportional to the interaction potential energy between the molecules^{1}.

Combining Eqs. (5) and (6), while neglecting terms of higher order than those linear in a and b, gives

$$PV = \frac{2}{3}E\left(1 + \frac{Nb}{V}\right) - \frac{N^2 a}{3V}.\qquad(7)$$

Applying Eq. (1) to Eq. (7) gives for the Grüneisen constant (i.e., energy derivative at constant volume) of the van der Waals' gas

$$\Gamma = \frac{2}{3}\left(1 + \frac{Nb}{V}\right).\qquad(8)$$

Eq. (8) contains the very important result that the intermolecular potential

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*Alternatively a and b may be considered as making up the second virial coefficient, say B_2, with

$$B_2 = Nb - \frac{Na}{kT}.$$

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(other than the approximately hard sphere interaction responsible for the volume exclusion constant b) does not appear in Γ . This is simply understood; at constant volume the average intermolecular distance remains unchanged by the addition of energy, and thus the potential energy from intermolecular interactions remains unchanged. We are thus led to expect that the intermolecular potential will not appear in the constant volume Grüneisen constant of a solid. Such is indeed the case.

Suprisingly enough Eq. (8) can be used to estimate the Γ of a liquid or a solid. One simple model for b has $b = 4V_0$, where V_0 is the volume of a molecule. Applying Eq. (8) to a solid or liquid with half of its available volume occupied by the molecules (and half otherwise empty), with the simple model for b mentioned above, yields

$$\Gamma = \frac{2}{3}\left(1 + \frac{4}{2}\right) = 2, \tag{9}$$

which is a suprisingly acceptable result; with the exception of Zirconium, metals have Grüneisen constants[2] which vary between one and three at room temperature and atmospheric pressure.

It is possible to understand the success of Eq. (9), as applied to a solid or a liquid, by considering the shock compression Hugoniot[3] EOS for a condensed medium. For volume changes small enough so that only the first nonlinear term need be considered we can write

$$P_H = A_H \left(\frac{\rho}{\rho_0} - 1\right) + B_H \left(\frac{\rho}{\rho_0} - 1\right)^2, \tag{10a}$$

or upon rewriting

$$P_H V = A'_H V_0 + B'_H \frac{V_0^2}{V} + C', \tag{10b}$$

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where the subscript zero denotes the undeformed state, the subscript H denotes Hugoniot, and A_H, B_H are characteristic of the material in question. ρ is the mass density, and the primed quantities are the constants associated with the rearrangement in Eq. (10b). The point of interest is that Eqs. (5) and (10b) have the same functional form (A_H is a function of temperature), and thus the proper interpretation of b in Eq. (8) should lead to a proper result -- which it does.

III. GENERAL THEORY

There are two ways in which to approach the problem of the Gruneisen parameter. One method involves purely macroscopic thermomechanical considerations, while the other involves a detailed statistical mechanics investigation of the system in question. We begin with the macroscopic approach.

A. Thermomechanical Considerations.

We start with the definition of Eq. (1). For V and T independent variables we have at constant volume

$$\Gamma = V \left(\frac{\partial P}{\partial E} \right)_V = V \left(\frac{\partial P}{\partial T} \right)_V \bigg/ \left(\frac{\partial E}{\partial T} \right)_V . \tag{11}$$

It is a simple problem in calculus to show [4], by alternatively considering V as a function of P and T, that

$$\left(\frac{\partial P}{\partial T} \right)_V = - \left(\frac{\partial P}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P$$

with the result

$$\Gamma = - V \left(\frac{\partial P}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P \bigg/ \left(\frac{\partial E}{\partial T} \right)_V . \tag{12}$$

The derivatives of Eq. (12) each relate to easily performed quasi-static (i.e., non shock) laboratory experiments:

$$\alpha \equiv \text{Thermal expansion coefficient} = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P , \tag{13a}$$

$$\beta \equiv \text{Bulk modulus} = - V \left(\frac{\partial P}{\partial V} \right)_T , \tag{13b}$$

$$C_V \equiv \text{Heat capacity at constant volume} = \left(\frac{\partial E}{\partial T} \right)_V \tag{13c}$$

In terms of α, β, and C_V, Eq. (12) becomes

$$\Gamma = \frac{\alpha \beta}{C_V} V . \tag{14}$$

In the absence of rate dependent effects for the energy deposition problem
(e.g., see the discussion relating to Fig. 1) the quasi-static result of Eq. (14)
theoretically should give the same Γ as that of the dynamic deposition experi-
ment. In practice such is not always true however, as the energy deposition
experiment measures Γ by measuring the pressure of the propagating shock
caused by that deposition, and effects such as attenuation and dispersion can easily
mask the correct induced pressure (and Γ).

There is another macroscopic approach of interest, especially since it is
related to work done in the next section. It happens that, to a good approximation
[5,6], the thermal properties of solid can be represented by its "characteristic
termperature", Θ . In that approximation the internal energy can be shown [5,6]
to be of the form

$$E = T f\left(\frac{\Theta}{T}\right),\tag{15a}$$

where f is a function with common form for all solids. Using the first law of
thermodynamics, and the definition of the free energy, F, of a system

$$F = E - T S,\tag{16}$$

where S is the entropy of the system, one can easily show

$$F = E + T\left(\frac{\partial F}{\partial T}\right)_V.\tag{17}$$

Eq. (17) says that F and E have the same functional form

$$F = T g\left(\frac{\Theta}{T}\right),\tag{15b}$$

where again g is a function with common for r for all solids.

Again using the first law of thermodynamics, along with Eq. (16), leads to

$$P = -\left(\frac{\partial F}{\partial V}\right)_T.$$ (18)

If we break up the internal energy into a zero temperature contribution, plus a temperature dependent part, then

$$E(V,T) = E_0(V) + E_1(V,T),$$ (19a)

$$F(V,T) = E_0(V) + E_1(V,T) - TS(V,T) \equiv F_c(V) + F_1(V,T),$$ (19b)

$$F_c(V) = E_0(V),$$ (19c)

where Eq. (19c) follows from (19b) and the third law of thermodynamics $(S \to 0$ as $T \to 0)$.

$$\therefore \; P = -\frac{\partial E_0}{\partial V} - \left(\frac{\partial F_1}{\partial V}\right)_T = -\frac{\partial E_0}{\partial V} - \left(\frac{\partial F_1}{\partial \Theta}\right)_T \left(\frac{\partial \Theta}{\partial V}\right),$$ (20)

where the second part of Eq. (20) follows from the characteristic temperature approximation as given by Eq. (15b).

Operating upon Eq. (15b) it is a simple matter to show that

$$\left(\frac{\partial F}{\partial \Theta}\right)_T = \frac{\partial g\left(\Theta/T\right)}{\partial\left(\Theta/T\right)},$$ (21a)

and thus

$$\frac{\partial\left(F/T\right)}{\partial\left(1/T\right)}\bigg|_V = \Theta\left(\frac{\partial F}{\partial \Theta}\right)_T.$$ (21b)

And using

$$\frac{1}{T}\frac{\partial F}{\partial\left(\frac{1}{T}\right)} = \frac{\partial\left(F/T\right)}{\partial\left(1/T\right)} - F$$ (22a)

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in Eq. (17) gives

$$\left(\frac{\partial F}{\partial \Theta}\right)_T = \frac{E}{\Theta} . \tag{22b}$$

Substituting Eq. (22b) into Eq. (20) yields

$$P = -\frac{\partial E_c}{\partial V} - \left(\frac{V}{\Theta}\frac{\partial \Theta}{\partial V}\right)\frac{E_1}{V} , \tag{23}$$

where we have applied Eq. (22b) to the temperature dependent contribution alone (subscript 1). For characteristic temperature models such as those of Debye and Einstein, which have a temperature independent Θ , comparing Eqs. (23) and (1) gives

$$\Gamma = -\frac{V}{\Theta}\frac{\partial \Theta}{\partial V} . \tag{24}$$

When the Debye characteristic Θ is used, Eq. (23) becomes the Debye EOS.

By using the functional details of a given Θ model, and experimental Hugoniot data in the form of Eq. (10a), we can thus use Eq. (24) to arrive at numerical values for Γ . Since the experimental Hugoniot data need not be from energy deposition experiments (it could be the result of explosive induced shock measurements), Eq. (24) turns out to be a very useful result. In the next section we shall see that

$$\Gamma = \frac{B_H}{A_H} \tag{25}$$

in terms of the coefficients of Eq. (10a).

B. <u>Statistical Mechanics Considerations.</u>

We immediately consider a system made up of two weakly interacting subsystems.

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As such the formalism is applicable to such systems as fluid filled porous solids[7], mechanical mixtures (e.g., KDNBF with diotomaceous earth - an explosive mixture sometimes used in electro-explosives devices), ard for at least conceptual purposes to electrons and phonons in solids.

Let $\mathbb{Z}$ be the partition function[8] for the system.

$$Z = \sum_{r,s} e^{-\beta E_{rs}} = \sum_{r,s} e^{-\beta(E_r + E_s + \mathcal{E}_{rs})} \, , \qquad (26)$$

where E_r is a total energy state of one of the subsystems, and $\mathcal{E}_{rs}$ is the inter-action energy between the two subsystems when one subsystem has energy E_r and the other has energy E_s. The sum is over all possible energy states consistent with the total energy of the system being constant. The interaction is assumed weak in that E_r and E_s are taken to be the subsystem energies in the absence of any interaction. The mean energy and entropy of the system are given in terms of Z by

$$\overline{E} = - \frac{\partial \ln Z}{\partial \beta} \, , \qquad (27a)$$

$$S = k(\ln Z + \beta \overline{E}). \qquad (27b)$$

Eqs. (26) and (27) are sufficient to find the free energy, and thus the pressure, and finally the Grüneisen parameter.

Using $\beta = (kT)^{-1}$, and further defining $\beta \mathcal{E}_{rs} << 1$ for a weak interaction, Eq. (26) becomes to first order

$$Z = \sum_{r,s} e^{-\beta E_r} e^{-\beta E_s} (1 - \beta \mathcal{E}_{rs}) \, , \qquad (28a)$$

or

$$Z = Z_A Z_B - \beta \sum_{r,s} \mathcal{E}_{rs} e^{-\beta E_r} e^{-\beta E_s} \, , \qquad (28b)$$

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where the subsystems are now labeled A and B, and Z_A is the partition function
of subsystem "A" when that subsystem is considered to be an isolated system.
Rewriting Eq. (28b)

$$Z = Z_A Z_B \left[1 - \frac{\beta}{Z_A Z_B} \sum_{r,s} \varepsilon_{rs} e^{-\beta E_r} e^{-\beta E_s} \right] \equiv Z_A Z_B Z_{AB} . \tag{29a}$$

Thus

$$\ln Z = \ln Z_A + \ln Z_B + \ln Z_{AB} , \tag{29b}$$

and

$$E \approx \bar{E} = \bar{E}_A + \bar{E}_B - \frac{\partial \ln Z_{AB}}{\partial \beta} . \tag{30}$$

Performing the last indicated operation in Eq. (30) gives

$$-\frac{\partial \ln Z_{AB}}{\partial \beta} = \frac{1}{Z_A Z_B} \sum_{r,s} \varepsilon_{rs} e^{-\beta E_r} e^{-\beta E_s} +$$
$$+ \frac{\beta}{Z_A Z_B} \sum_{r,s} \varepsilon_{rs} \left\{ \bar{E}_A + \bar{E}_B - E_r - E_s \right\} e^{-\beta E_r} e^{-\beta E_s} , \tag{31}$$

Similarly applying Eq. (27b) to Eq. (29b) yields

$$S = S_A + S_B + \frac{k\beta^2}{Z_A Z_B} \sum_{r,s} \varepsilon_{rs} \left\{ \bar{E}_A + \bar{E}_B - E_r - E_s \right\} e^{-\beta E_r} e^{-\beta E_s} , \tag{32}$$

and the free energy takes on the simple form

$$F = F_A + F_B + \frac{1}{Z_A Z_B} \sum_{r,s} \varepsilon_{rs} e^{-\beta E_r} e^{-\beta E_s} , \tag{33a}$$

or

$$F = F_A + F_B + F_{AB} , \tag{33b}$$

which defines F_{AB}. Although we could have guessed the result Eq. (33b) for two
weakly interacting subsystems, Eq. (33a) allows one to calculate F_{AB} when one has
a model for the subsystems and their interaction.

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C. General Applications.

Consider the case (e.g., a mixture of weakly interacting gases) when the subsystems can be considered as occupying the same volume. Then

$$P = - \left(\frac{\partial F}{\partial V}\right)_T = P_A + P_B - \left(\frac{\partial F_{AB}}{\partial V}\right)_T, \tag{34a}$$

or

$$PV = P_A V + P_B V - V\left(\frac{\partial F_{AB}}{\partial V}\right)_T, \tag{34b}$$

and

$$\Gamma E = \Gamma_A \bar{E}_A + \Gamma_B \bar{E}_B - V\left(\frac{\partial F_{AB}}{\partial V}\right)_T, \tag{34c}$$

where Eq. (1) has been used. The result Eq. (34c) is quite significant in that, even for non-interacting subsystems, it says that the Gruneisen parameter is a weighted average of the Gruneisen parameters of the subsystems. Eq. (34c) can, for example, be applied to problems such as the absorption of a high intensity laser beam by the air-vapor mixture in front of an irradiated solid surface[9].

Let us now apply Eq. (33b) to the case of a mechanical mixture, the subsystems (components) occupy volume separately. For brevity we neglect the interaction energy between the subsystems. Thus

$$F = F_A + F_B, \tag{35a}$$

$$V = V_A + V_B. \tag{35b}$$

$$\therefore P = - \left(\frac{\partial F}{\partial V}\right)_T = -\left(\frac{\partial F_A}{\partial V_A}\right)_T \frac{dV_A}{dV} - \left(\frac{\partial F_B}{\partial V_B}\right)_T \frac{dV_B}{dV}. \tag{36a}$$

Eq. (36a) contains the realistic assumption that F_A does not depend upon V_B, and similarly for F_B.

$$P = P_A \frac{dV_A}{dV} + P_B \frac{dV_B}{dV} , \tag{36b}$$

$$PV = \Gamma E = P_A V \frac{dV_A}{dV} + P_B V \frac{dV_B}{dV} , \tag{36c}$$

and then

$$\Gamma = \Gamma_A \left(\frac{\bar{E}_A}{E}\right)\left(\frac{V}{V_A}\frac{dV_A}{dV}\right) + \Gamma_B \left(\frac{\bar{E}_B}{E}\right)\left(\frac{V}{V_B}\frac{dV_B}{dV}\right). \tag{36d}$$

The result for a mixture of two non-interacting monatomic gases can be re-written, from Eq. (34c) and (2), as

$$\Gamma = \Gamma_A \left(\frac{N_A}{N}\right) + \Gamma_B \left(\frac{N_B}{N}\right) \tag{37}$$

an expected result. Eq. (36d) is thus reasonably explained as Eq. (37) plus a volume effect. We note that, for $N = N_A + N_B$, $\Gamma_A \leq \Gamma_B$ assumed, we have Γ varying linearly between the extremes Γ_A, Γ_B.

For the special case of components A and B undergoing equal strain (containing zero strain in both components as a special case), the solid mixture behaves as the gaseous mixture of Eq. (37). For equal strains

$$\frac{dV_A}{V_A} = \frac{dV_B}{V_B} , \tag{38a}$$

but

$$\frac{dV}{V} = \frac{V_A}{V}\left(\frac{dV_A}{V_A}\right) + \frac{V_B}{V}\left(\frac{dV_B}{V_B}\right). \tag{38b}$$

$$\therefore \frac{dV}{V} = \frac{dV_A}{V_A} = \frac{dV_B}{V_B}. \tag{38c}$$

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Using Eq. (38c) in Eq. (36d) yields

$$\Gamma = \Gamma_A \left(\frac{\bar{E}_A}{E}\right) + \Gamma_B \left(\frac{\bar{E}_B}{E}\right),$$

(39)

which has Γ varying linearly between Γ_A and Γ_B since $E = \bar{E}_A + \bar{E}_B$. We note that if the strains are equal the constant volume definition of Eq. (1) holds even for energy deposition pulse duration large compared to the time for acoustic propagation across a component particle; if the strains are equal they will be zero until a pressure wave due to inhomogeneous deposition reaches the local observation point. Thus for equal strains, which contains a statement concerning elastic constants, Eq. (39) appears to hold for energy deposition times both large and small compared to acoustic propagation times.

There is another special case which can be treated analytically. If the component strains are not equal (thus allowing local pressure relief), then for energy deposition times large compared to the time for acoustic propagation across a particle diameter

$$P = P_A = P_B,$$

(40a)

and

$$PV = P_A V = P_A V_A \left(\frac{V}{V_A}\right).$$

(40b)

$$\therefore \Gamma^* = \Gamma_A^* \left(\frac{\bar{E}_A}{E}\right)\left(1 + \frac{V_B}{V_A}\right),$$

(40c)

where Γ_A^* indicates the "effective" Grüneisen constant[10] since the constant volume conditions of Eq. (1) are not satisfied. Alternatively, Eq.(40a) can be used to substitute the compressibility, K, for the volume terms in Eq. (36d).

$$K = -\frac{1}{V}\frac{dV}{dP}.$$

(41)

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When Eqs. (40a) and (41) are used with Eq. (36d) one gets

$$\Gamma^* = \Gamma_A^* \frac{K_A \bar{E}_A}{K E} + \Gamma_B^* \frac{K_B \bar{E}_B}{K E} . \tag{42}$$

If the approximations of Eqs. (38c) or (40a) do not hold, then Eq. (36d) must be used along with a model for $V_A = V_A(V)$ and $V_B = V_B(V)$.

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IV. SOLIDS

In this section we consider the individual contributions to the Gruneisen parameter of a solid. We consider only metals because

a. The results for metals contain the results for dielectrics as a special case.

b. As mentioned in the introduction we have a strong interest in electromechanical effects in metals.

c. For the most part, aerospace materials are composed of metals, dielectrics, or their mixture (e.g., composites). Further, in present technology, aerospace applications stand the best chance of seeing an environment where a knowledge of the Grüneisen parameter is important.

We break up the problem into electron and phonon* contributions while neglecting the volume dependent zero degree Kelvin cohesive energy in keeping with the constant volume definition of Eq. (1). Thus

$$F(V,T) = F_e(V,T) + F_p(V,T) + \mathcal{E}_{ep}(V,T), \qquad (43)$$

where the subscript e denotes electrons, p denotes phonons, and $\mathcal{E}_{ep}(V, T)$ the contribution to the temperature dependent part of the free energy from electron-phonon interactions. Even though the interaction term appears to be crucial to the electromechanical problem, for the Gruneisen parameter problem one gets good agreement with experiment by considering the electrons and phonons to comprise non-interacting gases which occupy the same volume. Thus we neglect the interaction term and note that Eq. (34c) applies.

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*A phonon is a quantized unit of lattice vibration in a normal mode system where the vibrations behave as a set of non-interacting oscillators.

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A. Electrons.

From Zharkov and Kalinin [3] we have for the electron system

$$E_e(V,T) = \frac{2\pi^3}{3h^2} m \left(\frac{3N}{\pi}\right)^{1/3} V^{2/3} (kT)^2, \tag{44a}$$

$$S_e(V,T)T = \frac{4\pi^3}{3h^2} m \left(\frac{3N}{\pi}\right)^{1/3} V^{2/3} (kT)^2, \tag{44b}$$

$$\therefore F_e(V,T) = -\frac{2\pi^3}{3h^2} m \left(\frac{3N}{\pi}\right)^{1/3} V^{2/3} (kT)^2, \tag{44c}$$

$$\therefore P_e(V,T)V = \frac{4\pi^3}{9h^2} m \left(\frac{3N}{\pi}\right)^{1/3} V^{2/3} (kT)^2, \tag{44d}$$

$$\therefore \Gamma_e = \frac{2}{3} \tag{44e}$$

In the above m is the mass of an electron, N is the number of electrons in the system, and h is Planck's constant (h = 6.63 x 10^{-27} erg seconds). Comparing Eq. (44e) with Eq. (3) shows that the electrons behave as if they were an ideal gas. Eq. (44e) can also be derived on the more general grounds [11] of thermodynamics with a Planck distribution, which then gives Eq. (3) as a special case.

For the phonon contribution we break the problem up into low and high temperature regimes. The reason for the separation is the radically different functional dependence of the energy and entropy in the two regimes. The formulae for both regimes is from reference eleven.

B. Phonons-Low Temperatures.

$$E_p(V,T) = V \frac{\pi^2 (kT)^4}{10 (\hbar \bar{c})^3}, \tag{45a}$$

$$S_p(V,T)T = V \frac{2\pi^2 (kT)^4}{15 (\hbar \bar{c})^3}, \tag{45b}$$

$$\therefore F_p(V,T) = -V \frac{\pi^2 (kT)^4}{3 (\hbar \bar{c})^3}, \tag{45c}$$

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$$V P_p (V,T) = - V^2 \frac{\pi^2 \hbar (kT)^4}{10 (\hbar \bar{c})^4} \left(\frac{\partial \bar{c}}{\partial V} \right)_T \tag{45d}$$

$$\therefore \Gamma_p = - \frac{V}{\bar{c}} \left(\frac{\partial \bar{c}}{\partial V} \right)_T. \tag{45e}$$

In arriving at Eq. (45d) we have treated the factor of V in Eq. (45c) as a constant. This is because the factor of V tells how much material is present without saying anything about the structure, while the pressure is determined by the structure. The electron subsystem was treated in the same way in that the number of electrons, N, was taken to be constant. $h \equiv 2\pi \hbar$, and $\bar{c}$ is defined by

$$\frac{1}{\bar{c}^3} = \frac{1}{c_\ell^3} + \frac{2}{c_t^3} , \qquad \boxed{\text{Reproduced from best available copy.}} \tag{46}$$

where c_ℓ is the longitudinal sound velocity, and c_t is the transverse sound velocity.

C. Phonons - High Temperature.

At high temperatures the sums over the vibrational states become greatly simplified[11] with the result

$$E_p (V, T) = 3NkT, \tag{47a}$$

$$S_p (V,T) T = 3NkT \left[\ln kT - \ln \hbar \bar{\omega} + 1 \right], \tag{47b}$$

where N is the number of atoms (for brevity we consider a monatomic lattice) and $\bar{\omega}$ is some mean vibrational frequency associated with the lattice structure. It is obvious from Eqs. (47) that only the entropy contributes to the pressure.

$$\therefore PV = - 3NkTV \left(\frac{\partial \bar{\omega}}{\partial V} \right)_T , \tag{48a}$$

$$\therefore \Gamma_p = - \frac{V}{\bar{\omega}} \left(\frac{\partial \bar{\omega}}{\partial V} \right)_T. \tag{48b}$$

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If we now use the relationship from lattice dynamics [4]

$$\bar{\omega} = q \, \bar{c}, \qquad (49)$$

where q is the magnitude of the state vector $\vec{q}$, then we see that the high and low temperature regimes yield the same result

$$\Gamma_p = -\frac{V}{\bar{c}} \left(\frac{\partial \bar{c}}{\partial V} \right)_T . \qquad (45e)$$

A few words are in order regarding the difference between $\Gamma_e = 2/3$ and the result Eq. (45e). The energy of an individual phonon can be written

$$\mathcal{E} = p \, \bar{c}, \qquad (50)$$

where p is "momentum" associated with the phonon state. The form of Eq. (50) is radically different from that for the energy of a gas molecule in an ideal gas, namely,

$$\mathcal{E} = \frac{p^2}{2m} \qquad (51)$$

where m is the molecular mass. Thus the difference between Γ_e and Γ_p is explained by the non–gas-like behavior of the phonon system.

From the discussion of section II of this report we can assume that Γ_p is of order unity (we shall actually determine it later in this section), and apply Eq. (34c) with the interaction term taken as zero to judge the relative importance of the electron and phonon contributions. We need only consider the ratio $E_e(V, T)/E_p(V,T)$. The ratio is calculated below for $T = 300°K$ (high temperature limit), for the number of electrons equal to the number of vibrating atoms (i.e., a metal), and an electron density of 10^{21} per cm^3. The low temperature ratio is found to be unity at $10°K$.

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High Temp.:
$$\frac{E_e(V,T)}{E_p(V,T)} = \frac{2\pi^2 m k T}{3 h^2 \left(\frac{3n}{\pi}\right)^{2/3}} \sim \frac{1}{2c} \cdot \tag{52}$$

Low Temp.:
$$\frac{E_e(V,T)}{E_p(V,T)} = \frac{5 m h \left(\frac{3n}{\pi}\right)^{4/3} \bar{c}^3}{6\pi^2 (kT)^2} \sim 1 . \tag{53}$$

In Eqs. (52) and (53) we have taken a typical solid acoustic velocity, $\bar{c}$, of 5×10^5 cm per sec, and n is the density of electrons in the conduction band.

We thus see that a t room temperature only the phonon contribution is of importance, while below 10°K and above 6,000°K the electron and phonon contributions are of equal magnitude.

Let us now calculate Γ_p from experimental shock wave data. To do so we use Eqs. (10b), (45e), and

$$\bar{c}(\rho) \equiv \sqrt{\frac{\partial P_H}{\partial \rho}} . \tag{54}$$

In using Eq. (10b) for calculating Γ_p we are assuming that the density variation of P_H is primarily due to phonon effects. Since for metals the electron "sound" (i.e., Fermi) velocity [5] is of order 10^7 cm per sec, which is about a factor of 20 larger than the observed propagation velocity [3] for a weak shock, the assumption would appear to be valid. The assumption is also consistent with the discussion accompanying Eq. (52). The arithmetic is straightforward:

$$\bar{c}(\rho) = \left(\frac{A_H}{\rho_0}\right)^{1/2} \sqrt{1 + \frac{2 B_H}{A_H}\left(\frac{\rho}{\rho_0} - 1\right)} , \tag{55a}$$

$$\bar{c}(\rho) \approx \bar{c}_c \left\{ 1 + \frac{B_H}{A_H}\left(\frac{\rho}{\rho_0} - 1\right) \right\} , \tag{55b}$$

where
$$\frac{B_H}{A_H}\left(\frac{\rho}{\rho_0} - 1\right) \ll 1 \tag{55c}$$

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is assumed, and

$$\bar{c}_{\nu} \equiv \sqrt{\frac{A_H}{\rho}} \cdot$$

(55d)

$$\therefore \frac{V}{\bar{c}} \frac{\partial \bar{c}}{\partial V} \cong \frac{V}{\bar{c}} \frac{\partial}{\partial V} \left\{ \bar{c}_o \frac{B_H}{A_H} \left(\frac{V_o}{V} - 1\right) \right\} = - \frac{V}{\bar{c}} \left\{ \bar{c}_L \frac{B_H}{A_H} \frac{V_o}{V^2} \right\} \cdot$$

(55e)

$$\therefore \Gamma_p = \frac{B_H}{A_H} \quad ,$$

(25)

where we have evaluated Eq. (55e) at $V = V_0$.

Thus by using shock wave data generated by non-energy deposition experiments (e.g., flyer experiments), we arrive at a Grüneisen parameter for use in energy deposition induced shock work.

Table I below compares Γ_p for three metals from Eq. (25) with the Grüneisen parameter based upon the thermodynamic quantities of Eq. (14).

TABLE I

COMPARISON OF SHOCK AND THERMODYNAMIC DATA

Aluminum	2.17[a]	2.09[b]
Copper	2.00	1.98
Lead	2.78	2.46

[a] Hugoniot data from Table IV of reference 2.

[b] Values from L. V. Al'tshuler et al, Soviet Phys. J. E. T. P. 11, 573 (1960)

The agreement shown in Table I is rather good, and is typical of the agreement which one would get for a more extensive list of metals.

D. Volume Dependence.

It is also possible to include a volume dependence for Γ in the calculation leading to Eq. (25). One need simply not evaluate Eq. (55e) at $V = V_0$, and for higher volume terms simply add on additional higher order terms to Eq. (10b). The volume dependence of Γ is indeed quite important as can be seen from the data for aluminum (from ref. 2) given below

$$\Gamma(V) = 2.13 - 7.2\left(\frac{\rho}{\rho_0} - 1\right) + 25\left(\frac{\rho}{\rho_0} - 1\right)^2 . \qquad (56)$$

The volume terms of Eq. (56) contribute twenty percent to $\Gamma(V)$ for $\rho/\rho_0 = 1.2$, and the result would even be more impressive if the second and third terms on the right of Eq. (56) were not of opposite sign.

We should at this time comment on the physics of such a volume dependence, namely where it comes from. In Eq. (8) let b have a volume dependence (to be explained shortly), and expand Γ as a function of volume for a small volume change about an initial volume V_0. Thus

$$\Gamma(V_0 + \Delta V) = \Gamma(V_0) + \frac{2}{3}\left[\frac{db}{dV}\bigg|_{V_0} \frac{V_0}{b(V_0)} - 1\right] \frac{\Delta V}{V_0} . \qquad (57)$$

There are two contributions to Eq. (57). The first involves the volume change alone (i.e., $\Delta V/V_0$) and is explained by the observation that as the volume increases the molecular volume becomes less important; since pressure is a measure of the statistics of particle interactions with the walls of an imaginary container, the presence of other particles which occupy volume effects those statistics.

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The second contribution to Eq. (57) is proportional to (db/dV), and says that the molecular volume is dependent upon the density of neighboring molecules. This is understood by saying that where the volume dependence of the Grüneisen parameter is concerned, an exponential repulsive interaction is more appropriate than a hard sphere interaction. Indeed, by using such an exponential repulsive term Sirdeshmukh and Rao[12] were able to derive Γ (and its volume dependence) for some crystals of the fluorite structure.

Before leaving this section we wish to mention another method for arriving at the volume dependence of the Grüneisen parameter, namely the Dugdale - MacDonald formula[2,3]. That formula is

$$\Gamma = -\frac{V}{2}\frac{\partial^2(PV^{2/3})/\partial^2 V}{\partial(PV^{2/3})/\partial V} - \frac{1}{3}.\tag{58}$$

Eq. (57) is derived for an isotropic solid at $0°K$ by essentially taking the third derivative with respect to volume of the lattice potential energy (which is assumed to be only a function of the atomic coordinates). Eq. (58) works because, if ϕ is the potential energy, and if the potential is quadratic in the lattice parameter, then

$$\frac{\partial^3\phi}{\partial V^3} \propto \frac{\partial w}{\partial V},\tag{59}$$

$(w/2\pi)$ being the vibrational frequency of the $0°K$ unoccupied vibrational states. The success of Eq. (58) is understood as the right hand side of the proportionality, Eq. (59), is the prime ingredient of Eq. (48b).

Equation (58) is one of a whole class of relations[3] which utilize macroscopic PV data to arrive at a Grüneisen constant. All such relations, including Eq. (25)

and the procedure of this section used in deriving it, assume an isotropic solid. This means that the Hugoniot data used in arriving at Γ must be in a range where pressure is large compared to the yield stress (stress for the onset of plasticity). This is because most of the Hugoniot data is arrived at via one-dimensional strain experiments (e.g., flyer plate with planar geometry), with the result that solids are not in an isotropic state in the region of the yield stress[13]. The yield stress of a typical metal lies between a few kilobars and tens of kilobars.

E. Ultrasonic Data.

It frequently happens that Hugoniot data does not exist for a material. In such a case ultrasonic data can often be used to evaluate Γ. What is needed experimentally is the usual apparatus for measuring elastic constants, and additional equipment which allows for those measurements to be carried out as a function of pressure (a maximum pressure of a few kilobars is usually sufficient). The theory is relatively simple. If σ_{ij} is the stress tensor, then

$$\sigma_{ij} = C_{ijkl}\,\epsilon_{kl} + D_{ijklmn}\,\epsilon_{kl}\,\epsilon_{mn}, \qquad (60)$$

where ϵ_{kl} is the strain tensor, and C and D are the second order and third order elastic constants respectively[5]. For a cubic crystal undergoing an isotropic volume change, $P = \sigma_{11} = \sigma_{22} = \sigma_{33}$, and

$$\epsilon_{11} + \epsilon_{22} + \epsilon_{33} = \frac{V}{V_o} - 1. \qquad (61)$$

Thus the constants C and D can be related to the constants A_H and B_H of Eq. (10a). The D's are obtained through the pressure variation of the sound velocity. Eqs. (60) and (61) when combined are of the same form as Eq. (10b).

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While the Hugoniot EOS approach to the Grüneisen constant is valid for isotropic materials (e.g., polycrystalline metals) it is not valid for anisotropic single crystals [14]. This is because the Grüneisen parameter is really a second rank tensor and should be defined by

$$\Gamma_{ij} = V \left(\frac{\partial \sigma_{ij}}{\partial E} \right)_V \cdot \tag{62}$$

Eq. (1) is then seen to be Eq. (62) applied to isotropic solids. Since the C's and D's of Eq. (60) give all of the necessary information for evaluating the various elements of Γ, the ultrasonic method is the superior tool. Indeed application of the hydrostatic Hugoniot method to an anisotropic crystal such as Zirconium (hexagonal close packed) is now known [15] to give Γ values inconsistent with thermomechanical results because of anisotropic strain effects.

We are essentially making two points here. First, that in addition to the usual Hugoniot data, shock wave physicists have relevant ultrasonic data at their disposal. Second, that for anisotropic media, only the ultrasonic data is applicable.

V. DISCUSSION AND SUMMARY

The main intent of this report has been to give the shock wave physicist, the prime applied user of the Gruneisen parameter, an understanding of the physics involved in that parameter as well as the techniques in calculating it from related data.

In this closing section we make a few points which we hope will serve to tie up any loose strings. We also mention some relatively esoteric physics contributions to which at this time although interesting in their own right are relatively unimportant in applications.

Within the main text of this report we failed to mention the connection between the characteristic Θ Gruneisen parameter

$$\Gamma = - \frac{V}{\Theta} \frac{\partial \Theta}{\partial V} \, , \tag{24}$$

and that arrived at through phonon considerations

$$\Gamma_p = - \frac{V}{\bar{\omega}} \frac{\partial \bar{\omega}}{\partial V} \, . \tag{48b}$$

The connection is that the characteristic temperature Θ allows a characteristic frequency, $\omega_m/2\pi$, to be defined by

$$\hbar\omega_m \equiv k\Theta . \tag{63}$$

Thus if ω_m has the same volume dependence as $\bar{\omega}$ the two approaches will give the same result.

At high temperatures the detailed definition of $\bar{\omega}$ for a monatomic lattice is given by [11]

$$\log \bar{\omega} = \frac{1}{3N} \sum_i \log \omega_i \, , \tag{64}$$

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where α is an index over the possible vibrational states of the solid. The allowed number of ω_α increase as ω_α^3 (a relationship known as the density of states [11]) so that we expect $\bar{\omega} \approx \omega_m$ as ω_m is associated with the highest possible energy state for a characteristic Θ model. Thus we are led to expect equality in the two approaches at high temperatures.

At low temperatures a probability factor is present (relating to the probabiltiy that a given state is occupied [11]) in the equivalent of Eq. (63). This probability factor serves to reduce the ratio $\bar{\omega}/\omega_m$ to zero as the temperature goes to zero. Since $\bar{\omega}$ is no longer close to ω_m they do not necessarily have the same volume dependence – and indeed for many materials they do not have the same volume dependence.

Germanium offers a good example of the complications introduced by low temperatures. Experimentally the thermomechanical Gruneisen parameter, Eq. (14), of Germanium is negative [14] in the region between 10°K and 40°K. Yet $\frac{\partial \omega_m}{\partial V}$ is determined only by the crystal structure and remains positive in that same region. That low temperatures present difficulties should not be suprising as we have already seen that electron contribution to Γ is equal to the phonon contribution at about 10°K. Those interested in further details of the electronic contributions to are referred to the work of Wallace [16].

There is another conceptual approach to the physics of the Grüneisen parameter which is very much worth mentioning. It is correct to think of phonons and electrons as representing thermally excited states of a crystal lattice in the same sense as kinetic energy is the thermal excitation of an ideal gas. But there are a host of other possible excited states in a crystal lattice which are more or less important

depending upon temperature, volume, and the types of atoms making up the crystal in question. Some of these thermal excitations are listed below.

MAGNONS[5] — elementary propagating magnetic waves in paramagnetic materials.

EXCITONS[5] — coupled electron-hole pair states.

ROTONS[17] — elementary rotational states in a superfluid.

ELECTRON-ELECTRON PAIRS[5] — the elementary excitations responsible for superconductivity.

HELICONS [18] — an electromagnetic excitation in a solid state plasma.

The point is that each type of thermal excitation represents a mechanism for storing energy. Like electrons and phonons the energy dependence of the partial pressures contributed by those more exotic excitations must be considered in evaluating the Gruneisen parameter.

The effect of the more exotic excitations is presently not a serious question for the applied shock wave physicist. However, as environments change and previously strange materials are introduced into technology .....

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